United States Patent [19]

Raynolds

[11] **3,896,088**

[45] **July 22, 1975**

[54] **FLUORINATED OILY SOIL RELEASE AGENTS**

[75] Inventor: **Stuart Raynolds,** Wilmington, Del.

[73] Assignee: **E. I. du Pont de Nemours and Company,** Wilmington, Del.

[22] Filed: **Nov. 24, 1972**

[21] Appl. No.: **309,447**

[52] **U.S. Cl.**..... **260/70 R;** 117/139.4; 260/70 A; 260/70 M; 260/71; 260/309.7; 260/849

[51] **Int. Cl.**..... **C08g 9/36**

[58] **Field of Search**..... 260/849, 70 R, 70 A, 70 M, 260/71, 309.7

[56] **References Cited**

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Primary Examiner—John C. Bleutge

[57] **ABSTRACT**

An adduct is prepared by heating together, in the presence of an acid catalyst, (1) a perfluoroalkyl carbamate of formula $R_f(CH_2)_n—O_2C—NH_2$ such as perfluoroalkylethyl carbamates; (2) a polyalkylene oxide glycol such as polyethylene oxide glycol having a molecular weight of about 1,000; and (3) a dialkoxymethylethylene urea such as N,N'-bis(methoxymethyl-)ethylene urea. These adducts are effective in promoting oil and water repellency and oily soil release from textiles.

5 Claims, No Drawings

FLUORINATED OILY SOIL RELEASE AGENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to new compositions which when applied to textile substrates confer oil and water repellency and improved washability to said substrates, enhancing the removal therefrom of oily stains. More particularly this invention is directed to the adducts formed by the reaction of a perfluoroalkylethyl carbamate, a polyalkylene oxide glycol and a N,N'-bis(alkoxymethyl)ethylene urea and the use of such adducts as oily soil release agents for textiles.

2. Prior Art

Textiles are routinely treated to enhance desirable properties and minimize undesirable properties. Synthetic fabrics and fabrics composed of blends of natural and synthetic fibers have good strength and resistance to abrasion, and also sufficient resilience to allow shape retention when worn or otherwise distorted in use. Such fabrics are often treated with finishing agents to give them a softer "hand" or feel. Cotton fabrics normally have a good hand but are often treated to increase fiber resilience and crease resistance.

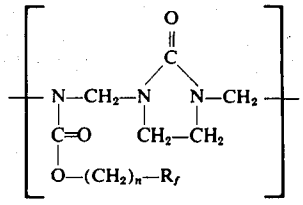
Fabrics, particularly cotton containing fabrics, are often treated with thermosetting organic resins to give them permanent press characteristics. In addition to the thermosetting resin, catalysts and various modifying additives or finishing agents such as softeners, antistatic agents, etc., are also used to provide suitable commercial fabrics. Many of such treated fabrics have good wearing characteristics but the tendency of the fiber to accept oily stains is increased, and the ability of the material to release such stains upon laundering is usually reduced. "Wicking" or diffusion of the stain into the bulk of the fabric makes the stain even more difficult to remove. An improvement in the resistance of the fabric to staining can be provided through treatment with agents which impart oil and water repellency. However, oily stains can still occur despite these treatments, when oil or oily materials are forced into the fabric, such as may result from pressure or prolonged contact. The ability of the material to release this sort of stain is inhibited by the fluorochemical treating agents. The most serious problem with wash and wear and permanent press fabrics is the permanent kind of stain which cannot be removed by conventional home laundering.

Thus the prior art treatments for promoting oily soil release suffer from various shortcomings. Some treatments are effective for a while but do not retain their effectiveness through repeated launderings. The cost of any such treatment must, of course, be weighed against the value of improvement attained.

An object of this invention is to provide a composition for treating fabrics to endow said fabrics with greater oily stain release on laundering. A further object of the invention is to provide textile treating agents which confer oil repellency in normal wear, are durable and stable to repeated launderings, and which release oily stains and soil during laundering of the treated fabric. Other objects will become evident from out disclosure.

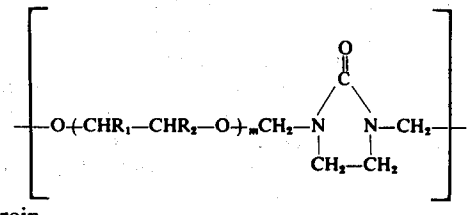
SUMMARY

In summary, this invention is directed to an adduct containing recurring units



wherein

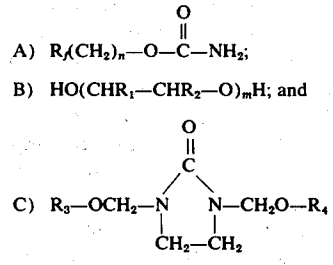
n is an integer of from 1 through 12 and R_f is perfluoroalkyl of from 4 through 16 carbon atoms; and



wherein

m is an integer of from 10 through 300, R_1 is hydrogen or methyl and R_2 is hydrogen or methyl with the limitation that at least one of R_1 and R_2 is hydrogen;

prepared by condensing in the presence of an acid catalyst



wherein

m, n, R_f, R_1 and R_2 are as defined above,

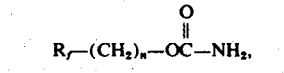
R_3 is alkyl of from 1 through 4 carbon atoms and R_4 is alkyl of from 1 through 4 carbon atoms;

wherein the molar ratio of A to B is from about 0.25:1 to 9:1, and the molar ratio of A + B to C is from about 0.6:1 to 1.5:1.

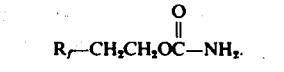
These adducts provide a durable, launderable treatment employing reasonably low add-on for effectiveness with an economical, easily manufactured new adduct.

DESCRIPTION OF THE INVENTION

The adducts of this invention are derived from three classes of bifunctional compounds. The first of these is composed of carbamates having a perfluorinated hydrocarbon component of the structure

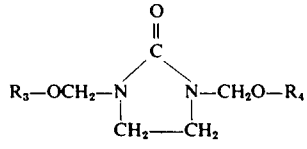


wherein R_f and n are as defined above. The preferred carbamate has the formula



Bifunctionality of the carbamates is due to the two active hydrogens of the $-NH_2$ group.

The second class of compounds is composed of N,N'-bis(alkoxymethyl)ethylene ureas of the formula



wherein R_3 and R_4 are as defined above. The preferred of these is N,N'-bis(methoxymethyl)ethylene urea. Bifunctionality of these compounds is due to the two rather labile alkoxy groups which react with active hydrogens under acid conditions to form alcohols.

The third group of components is composed of polyalkylene oxide glycols, preferably polyethylene oxide glycols of molecular weight from 200 to 4,000, most preferably about 1,000 to about 1,800. These compounds possess bifunctionality due to the active hydrogen of the hydroxy groups at each end of the molecule.

In preparing the adducts of this invention the three primary components are preferably mixed in the presence of an inert diluent and a mildly acidic catalyst. The inert diluent will preferably form an azeotrope with the alcohol released during the reaction so that said alcohol can be easily removed from the reaction mass by azeotropic distillation. Examples of satisfactory diluents are 1,1,2,2-tetrachloro-1,2-difluoroethane, benzene, toluene and carbon tetrachloride. The diluent is not essential to the reaction and can be omitted, the alcohol of reaction being removed by direct distillation, conveniently under reduced pressure.

The catalyst serves to speed the reaction, while the removal of the alcohol product urges it to completion. A preferred catalyst is formed by reacting chemically equivalent quantities of p-toluenesulfonic acid and dimethyldodecylamine to produce the dimethyldodecylamine salt of p-toluenesulfonic acid.

To prepare the adduct the ingredients are agitated together and the temperature slowly raised to the distillation temperature, which will normally be between 50° and 150°C. The distillate is removed, and distillation is continued until a pre-determined amount of alcohol has been removed. The distillation is then continued to remove most of the inert diluent. If desired, all of the diluent can be removed; however, for ease of handling enough can be left in the reaction mass to allow it to be easily poured or pumped. Usually a mixture containing about 80% reaction product and 20% diluent has been found convenient to manipulate.

In order to prepare a dispersion for easy handling and measuring, water is added in an amount sufficient to produce a mixture containing 15–30% of the active ingredient adduct. The mixture is dispersed in a high shear mixing device. In application to textile materials the adduct must be used in conjunction with a melamine resin of the group commonly used as crease-resistant agents. An example is "Aerotex" 23 Special, a product of American Cyanamid Co. The acidic catalyst commonly employed in conjunction with the use of melamine resins as crease-resistant agents is also used, magnesium chloride and zinc nitrate being familiar examples.

Because of the aqueous solubility of the adducts of this invention, they are effective only when applied to substrates in conjunction with a melamine resin as described. Co-application fixes the polymer to the fabric and results in durable oil and water repellency and oily stain release during laundering.

After application to the fabric or other substrate, usually at a level of 0.25 to 3% of the polymer and about 0.2 to 1% of the commercial melamine resin product, based on dry fabric weight, the treated material is dried and cured under the conditions normally employed to dry and cure crease-resistant agents. For example, the treated material can be dried for a few minutes at about 250°F., and then cured for about 2 to 4 minutes at about 325°F. The fabric thereafter exhibits improved oil repellency, and oily stains are effectively removed by normal home laundry procedures.

Textiles which are suitable substrates for treatment with the adducts of this invention include natural materials such as cotton and wool which have been pretreated with chemicals to improve shrink or crease resistance, and synthetics such as polyamides, polyesters and the like. Particularly suitable are polyesters and their blends with cotton.

Of the three classes of materials used to prepare the adducts of this invention, only the one comprising polyethylene oxide glycols is readily availabe commercially in a large range of molecular weights; i.e., "Carbowax," available from Union Carbide Corp. wherein Carbowax 1000 has a molecular weight of about 1,000, Carbowax 300 has a molecular weight of about 300, etc,; the "Pluracol" line of polypropylene oxide glycols obtainable from the Wyandotte Chemical Co. in a large range of molecular weights; and "Propylene Glycols" obtainable from the Union Carbide Corp.

Methods for preparing polyfluoroalkyl carbamates are disclosed in British Pat. No. 1,231,946 beginning on page 1, column 2, line 69.

The preferred polyfluorohydrocarbyl carbamate is prepared from the corresponding polyfluorohydrocarbyl alcohol (disclosed in Example 1 of U.S. Pat. No. 3,378,609) by ester interchange with a commercially available alkyl carbamate such as ethyl carbamate, using a tetraalkyl titanate ester as catalyst. The reaction may be written thus

$$R_f-CH_2CH_2OH + C_2H_5OC(=O)-NH_2 \xrightarrow{\text{tetraisopropyl titanate}} R_f-CH_2CH_2OC(=O)-NH_2 + C_2H_5OH\uparrow$$

where R_f is as defined hereinbefore.

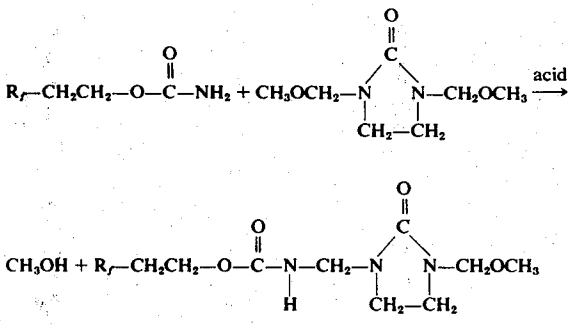
Compounds of the third class, the N,N'-bis(alkoxymethyl)ethylene ureas, are made by reacting ethylene urea with formaldehyde under alkaline conditions to produce dimethylol ethylene urea, then reacting the product with an alkanol, preferably methanol, to produce a bis(alkoxymethyl)ethylene urea. The final product can be purified by distillation if desired, but is ordinarily pure enough for use without distillation.

In combining the three components, the order of mixing or reaction is not of great importance. All three components can be introduced into a reaction vessel at the same time, or for instance the polyfluorocarbamate

and bis(alkoxymethyl)ethylene urea can be partially reacted and the polyalkylene oxide glycol introduced thereafter and further reacted until reaction is complete.

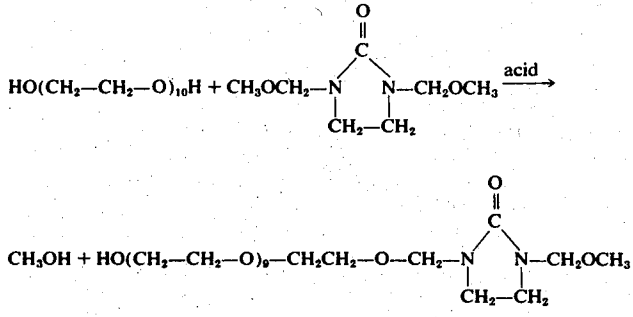
The reactions which occur depend mainly on the reactivity of the alkoxy groups of the bis(alkoxymethyl-)ethylene urea under acid conditions. The alkoxy group reacts with active hydrogen containing compounds to split off the corresponding alcohol as shown in the following equation:

(1)



Of course a second molecule of the carbamate can react with the second methoxy group of the bis(methoxymethyl)ethylene urea also. Likewise the polyalkylene oxide glycol can react with the bis(methoxymethyl)ethylene urea as shown in equation (2) below

(2)

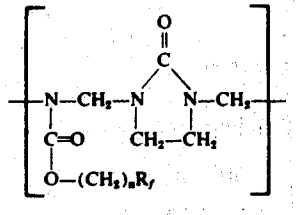


A second molecule of polyethylene oxide glycol can react with the second methoxy group of the bis(methoxymethyl)ethylene urea. The reaction thus produces a mixture of products in which the illustrated linkages appear, and in which most of the reactive hydrogens present have reacted with the alkoxy groups of the bis(alkoxymethyl)ethylene urea, as indicated by the removal of a nearly theoretical amount of alcohol.

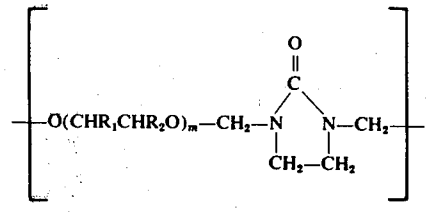
The perfluoroalkyl carbamate and the polyalkylene oxide glycol do not react with each other under the conditions employed.

Thus the adduct will contain segments corresponding to the following formulas, a and b, but without an identifiable regular or repetitive pattern of placement in the adduct chain -

a)



b)

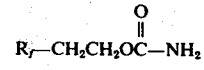


wherein R_f, m and n are as defined hereinbefore.

Since the polyalkylene oxide glycol and perfluoroalkyl carbamate do not self-condense, each of these molecules has a methylenthylene urea on each side, separating it from the next glycol or carbamate molecule. Each unit containing the perfluoro group thus contains only one such group associated with a hydrophilic methylethylene urea group.

The adducts which have been found most effective are prepared from mixtures where the molar ratio of the polyfluorocarbamate to the polyalkylene oxide alycol is between about 0.25:1 and about 9.0:1, and the molar ratio of the sum of these two to the bis(alkoxymethyl)ethylene urea is between about 0.6:1 and about 1.5:1. In terms of A, B and C as previously written A/B is 0.25 – 9 and (A + B)/C is 0.6 – 1.5.

A particularly preferred adduct is prepared from (A) 2 moles of



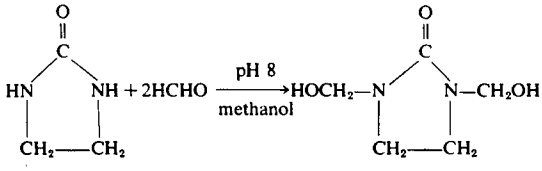
where R_f contains 6–14 carbons, (C) 3 moles of bis(methoxymethyl)ethylene urea, and (B) 1 mole of $HO(CH_2CH_2O)_{35}H$ commercially available as "Carbowax" 1540. Thus the molar ratio of A/B is 2.0 and the ratio of (A + B)/C is 1.0.

The following examples illustrate the invention. Parts and percentages in the examples are by weight unless otherwise specified.

EXAMPLE 1

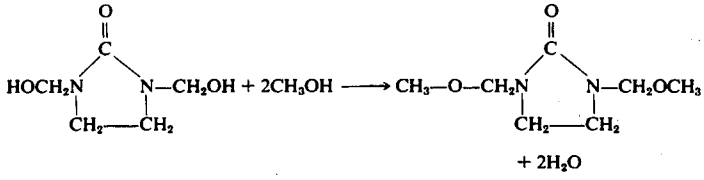
Preparation of Bis(methoxymethyl)ethylene Urea

In a vessel fitted with agitator, thermometer and distilling condenser were mixed 12.9 parts of ethylene urea, 11.4 parts of paraformaldehyde and 39.5 parts of anhydrous methanol. The pH was adjusted to 8.0–8.2 by adding 5% methanolic sodium hydroxide. The mass was stirred at about 50°C. for an hour and an additional 9.0 parts of methanol were added. At this time the first reaction was essentially completed according to the following equation:

(3) 

At about 25°C. there was then added a solution of 0.4 part of concentrated hydrochloric acid (37%) in 1.5 parts of methanol, and the mixture was stirred for 1 hour at 20°–25°C. The pH during this phase was 4.0. After 1 hour stirring the pH was again adjusted to about 8 with 10% methanolic sodium hydroxide and stirring continued for one-half hour at 20°–15°C. The preparation was then allowed to stand without agitation for 16 hours (overnight). Upon standing the reaction mixture separated into 2 layers, a top layer of clear solution and a bottom layer containing a finely divided solid. The entire mass was filtered and the solids washed with a little methanol, the washings being combined with the filtrate.

Methanol and water of reaction were removed by heating the liquid at reduced pressure in a suitable system under nitrogen. The precipitated solid (sodium chloride) was removed by filtration. The second reaction was as shown in the following equation:

(4) 

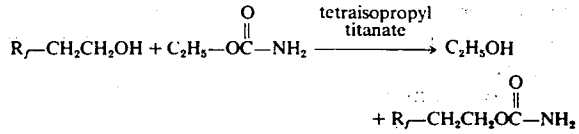
The yield of crude product was 13.3 parts, essentially 100%. If desired, the product could be distilled under vacuum, thereby separating any high boiling impurities.

EXAMPLE 2

Preparation of Perfluoroalkylethyl Carbamate

Into a suitable vessel fitted with a thermometer, agitator and short fractionating column was charged 35.0 parts of $R_f—CH_2CH_2OH$, where R_f is a mixed perfluoroalkyl of 6, 8, 10 and 12 carbon atoms, and 7.5 parts of dry toluene. The charge was heated to the boil, and traces of water and other low boiling impurities removed by fractional distillation at atmospheric pressure. The total distillate removed was 1.05 parts. The temperature in the reaction vessel during the fractionation was about 125°C. and the temperature at the top of the fractionating column was about 105°–108°C.

After cooling to 75°C. 6.96 parts of ethyl carbamate were added as was 0.035 part of tetraisopropyl titanate. The charge was then heated gradually to a temperature of 128°C., as low boiling products were continuously removed via the fractionating column. The distillation and reaction were continued over a period of several days, the reactor being shut down at night under a nitrogen blanket. An additional 0.085 part of tetraisopropyl titantate catalyst was added in several parts over the total period. The reaction equation is as follows:



When no more ethyl alcohol was evident in the distillate, the reaction mass was cooled to room temperature under nitrogen. Overnight the charge solidified in the reaction vessel. It was then melted, and 0.17 parts of water and 0.75 part of filter aid were added and the charge was then filtered through filter paper using a heated filter. The material retained on the filter was washed with about 10.0 parts of hot (100°C.) toluene, an the washes were combined with the filtrate.

The filtered reaction product was heated under reduced pressure to melt it and to remove residual toluene. The product was poured into flat pans and allowed to solidify. The yield was 34.9 parts, about 91.4% of theory, based on the perfluoroalkyl alcohol, where the average molecular weight of $R_f—CH_2CH_2OH$ was 470.

EXAMPLE 3

Preparation of Adduct

A catalyst was first prepared by mixing 21.3 parts of dodecyldimethylamine ("Armeen" DM12D) and 17.2 parts of p-toluenesulfonic acid monohydrate and heating the product to dissolve in 50 parts of toluene, then cooling and isolating the crystallized salt by filtration. Alternatively the catalytic effect can be obtained by charging to the reaction equivalent amounts of the same two reactants in the desired amount.

To a suitable vessel equipped with thermometer, agitator and short fractionating column were charged 40.6 parts of the carbamate product of Example 2 and 20.9 parts of the bis(methoxymethyl)ethylene urea derivative of Example 1 plus 61.2 parts of "Carbowax" 1540, a product of Union Carbide having the formula $HO(CH_2CH_2O)_{35}H$, and 0.2 part of the above prepared catalyst. Also charged to the vessel were 200 parts of 1,1,2,2-tetrachloro-1,2-difluoroethane, an inert diluent boiling at 92°C.

The mixture was heated to the boil at atmospheric pressure with agitation, and low boiling reaction products (primarily methanol) removed through the fractionating column. The temperature at the top of the column rose gradually to 90°C. over about 4 hours and held at this temperature for an additional 2 hours. The yield of the resulting adduct was 116.2 parts. Sufficient diluent was removed by distillation to leave a mixture containing 80% product. A slurry containing 78 parts water and 22 parts of the 80% adduct mixture was agitated at high speed (in a Waring blender) for about 10 minutes, producing a uniform, stable dispersion. The dispersion was adjusted to 17.0% solids content by agitating briefly with an additional weighed amount of water. The dispersion was then in suitable form for use in treatment of textile material.

EXAMPLE 4

The adduct preparation of Example 3 was repeated with two changes. Benzene was used as inert diluent and, instead of preparing the p-toluenesulfonic acid salt, the free acid monohydrate and amine were separately charged to the reaction in chemically equivalent amounts.

To a suitable vessel were charged 40.6 parts of the carbamate product of Example 2, 20.9 parts of the bis(methoxymethyl)ethylene urea derivative of Example 1, 61.2 parts of Carbowax 1540, 129 parts of dry benzene, 0.3 part of p-toluenesulfonic acid monohydrate and 0.41 part of dodecyldimethylamine, Armour Company's "Armeen" DM12D. The charge was heated with agitation, and the alcohol of reaction removed by azeotropic distillation with benzene. After completion of the reaction there remained in the reactor 164.7 parts reaction mass containing 69.5% adduct product. A working dispersion containing 15.35% adduct was prepared as in Example 3, using 34 parts of the reaction mass and 120 parts of water.

EXAMPLE 5

Application and Testing

An aqueous dispersion was prepared containing weighed amounts of the 15.35% adduct dispersion of Example 4, 21.1%; "Aerotex" 23 Special, American Cyanamide's melamine-uron resin, 50% solution, 1.3%; and American Cyanamide's "Accelerator" MX, a 25% aqueous solution of magnesium chloride curing catalyst, 0.26%. A weighed piece of 100% polyester double knit fabric was dipped in the prepared dispersion and passed through a wringer, then dipped and wrung again, giving a pick-up of the dispersion amounting to 77% of the weight of the dry cloth. Removal of the water by drying left 0.38% of the polymer of Example 4, 0.5% of the melamine resin and 0.05% magnesium chloride catalyst, all based on dry fabric weight. The fabric was dried 4 minutes at 250°F., then cured in a 320°F. oven for an additional 3 minutes.

The treated cloth was tested for oil repellency, water repellency and for soil release. The tests were repeated after 5 home launderings.

The oil repellency test is the Americal Association of Textile Chemists and Colourists Standard Test Method 118—1966.

The water repellency test is the American Association of Textile Chemists and Colourists Standard Test Method 22—1952 (ASTM D-583-63).

Oil Repellency Rating	Test Solution	Surface Tension Dynes/cm. at 25°C.
9	n-Heptane	20.0
8	n-Octane	21.8
7	n-Decane	23.5
6	n-Dodecane	25.0
5	n-Tetradecane	26.7
4	50–50 hexadecane-Nujol	28.7
3	25–75 hexadecane-Nujol	30.3
2	Nujol	31.2

Home Laundering Test

A Kenmore washer Model 600 is loaded with a 4-lb. load, with 29 g. of Tide. The wash is set at hot (12 min. cycle) and a warm rinse (12 min.). The total washing and rinsing time is 40 minutes. In the home laundering air dry test, the spun dry fabrics are dried at ambient temperatures. In the home laundering tumble-dry procedure, the spun dry fabrics are dried at 156°–160°F. in a home drier with tumbling.

The soil release test is described in Textile Chemist and Colourist 3 No. 10, October (1971).

Results are shown in Table I. Soil release in this table and the others of this application is 1,000 times W, soiling value of the washed fabric, of the reference article. The lower the number the more easily the soil is removed in the wash test. The numbers have no absolute value, but are compared in each test with a blank subjected to the same soiling treatment.

TABLE I

	Treated Sample of Example 5	Untreated Cloth
Initial Soil Release	11	329
Oil Repellency	6	0
Water Repellency	70	50
After 5 Home Washes -		
Soil Release	33	292
Oil Repellency	4	0
Water Repellency	70	70

EXAMPLES 6–14

A series of polymer preparations was made according to the general method of Example 3. In this series preparations and conditions were held constant except that the ethylene oxide polymer employed varied in molecular weight from about 200 to about 1,000 and the weight ratio of fluorocarbamate to ethylene oxide polymer varied from 70/30 to 90/10. The fabric used was 100% polyester double knit.

TABLE II

Example No.	Wt. Ratio Carbamate/ Ethylene oxide Polymer	MW Ethylene oxide Polymer	Oil Repellency Initial	Oil Repellency After 5 Washes	Water Repellency Initial	Water Repellency After 5 Washes	Soil Release Initial	Soil Release After 5 Washes
6	70/30	200	4	0	0	70	−8	151
7	70/30	600	5	0	0	0	−14	57
8	70/30	1000	5	0	0	0	−15	43
9	80/20	200	5	1	0	70	20	145
10	80/20	600	5	0	0	70	9	42
11	80/20	1000	5	1	0	70	12	42
12	90/10	200	5	1	0	70	11	148
13	90/10	600	6	0	0	70	22	95
14	90/10	1000	6	2	0	70	10	85
Untreated fabric	—	—	0	0	0	0	401	581

The series of experiments indicates that the higher the molecular weight of the ethylene oxide, the better the results in terms of soil release, other conditions being as indicated.

EXAMPLE 15

An adduct of the invention was prepared in a two-step procedure employing as catalyst the prepared salt of dodecyldimethylammonium-p-toluene sulfonate described in Example 3 and also 1,1,2,2-tetrachloro-1,2-difluoroethane as inert diluent for the reaction. Pluracol 1010, a polypropylene oxide glycol of about 1,010 molecular weight was used in place of the polyethylene oxide glycol used in Example 3.

To a suitable vessel equipped with thermometer, agitator and short fractionating column were charged 5.22 parts of bis(methoxymethyl)ethylene urea, 10.26 parts of the perfluoroalkylethyl carbamate of Example 2, **0.023** part of the prepared catalyst salt of Example 3 and 163.7 parts of 1,1,2,2-tetrachloro-1,2-difluoroethane. The charge was agitated and heated to distil methanol of reaction and remove it as an azeotropic mixture with the tetrachloro-difluoroethane. In this step there were removed 10.0 parts of distillate containing 1.28 parts of methanol. The charge was cooled to about 25°C. and 9.5 parts of Pluracol 1010 were added, and distillation was resumed. In this second step there were removed 8.2 parts of distillate containing 0.53 part of methanol. The material remaining in the flask contained 14.8% adduct equivalent to 25.2 parts. The inert diluent was removed by distillation and the solid adduct was combined in a Waring blender with 29.6 parts of 1,1,2,2-tetrachloro-1,2-difluoroethane and 45 parts of 10% aqueous isopropanol. A stable emulsion resulted.

The adduct was tested for oil and water repellency and for soil release as described in Example 5. The treated polyester double knit fabric retained after drying, based on weight of the dry fabric, 0.153% of the solid adduct, 0.65% of the melamine-uron resin as Aerotex 23 Special, a 50% melamine resin solution, and 0.065% of magnesium chloride as Accelerator MX, 25% magnesium chloride solution. The treated fabric was dried for 4 minutes at 250°F. then cured for 3 minutes in a 320°F. oven. Results of oil repellency, water repellency and soil release tests are shown in Table III below.

TABLE III

	Sample of Example 15	Untreated Cloth
Initial Soil Release	61	222
Oil Repellency	5	0
Water Repellency	70	0
After 5 Home Washes -		
Soil Release	246	448
Oil Repellency	2	0
Water Repellency	70	0

EXAMPLE 16

To a flask fitted with agitator, thermometer and fractionating column there were charged the following:

a. Fluorocarbamate product of Example 2, 40.6 parts (0.08 mole or 0.16 equivalents),

b. Carbowax 6000 [$HO(CH_2CH_2O)_nH$] molecular weight about 6,000, 61.2 parts (0.01 mole or 0.02 equivalents),

c. Bis(methoxymethyl)ethylene urea, 15.7 parts (0.09 mole or 0.18 equivalents),

d. Prepared catalyst salt of Example 3, 0.2 part,

e. 1,1,2,2-Tetrachloro-1,2-difluoroethane, 327.4 parts.

The mixture was heated to the boil at atmospheric pressure under agitation, and methanol of reaction removed by azeotropic distillation. When no more methanol appeared in the distillate, the charge was cooled and 0.2 part sodium bicarbonate added to neutralize the acidic catalyst. The total methanol distilled was 5.7 parts. The volatile solvent material was removed by distilling under slightly reduced pressure, distillation being terminated when pot temperature was 65°C. at 710 mm. pressure. When removed from the flask there was isolated 119.0 parts of adduct product which solidified as it cooled.

This adduct utilized a mol ratio of A/B of 8.0 and a mol ratio of (A + B)/C of 1.0.

EXAMPLE 17

The procedure of Example 16 was repeated employing the following materials:

a. Fluorocarbamate product of Example 2, 40.6 parts,

b. Carbowax 20M [$HO(CH_2CH_2O)_nH$] molecular weight about 20,000, 61.2 parts (0.003 mole or 0.006 equivalents),

c. Bis(methoxymethyl)ethylene urea, 14.5 parts (0.083 mole or 0.166 equivalents),

d. Prepared catalyst of Example 3, 0.2 part,

e. 1,1,2,2-Tetrachloro-1,2-difluoroethane, 327.4 parts.

Upon isolation, 138.6 parts of the adduct product were recovered. This adduct utilized a mol ratio of A/B of 26.6 and aa mol ratio of (A + B)/C of 1.0.

EXAMPLE 18

The procedure of Example 16 was repeated employing the following materials:

a. Fluorocarbamate product of Example 2, 40.6 parts,

b. Carbowax 1540 [$HO(CH_2CH_2O)_nH$] molecular weight about 1540, 61.2 parts (0.04 mole or 0.08 equivalents),

c. Bis(methoxymethyl)ethylene urea, 12.5 parts (0.072 mole or 0.144 equivalents),

d. Prepared catalyst of Example 3, 0.2 part,

e. 1,1,2,2-Tetrachloro-1,2-difluoroethane, 327.4 parts.

Upon isolation, 109.7 parts of the adduct product were recovered.

This adduct utilized a mole ratio of A/B of 2.0 and a mole ratio of (A + B)/C of 1.7.

EXAMPLE 19

The procedure of Example 16 was repeated employing the following materials:

a. Fluorocarbamate product of Example 2, 40.6 parts,

b. Carbowax 1540 [$HO(CH_2CH_2O)_nH$] molecular weight about 1,540, 61.2 parts (0.04 mole or 0.08 equivalents),

c. Bis(methoxymethyl)ethylene urea, 31.3 parts (0.18 mole or 0.36 equivalents),

d. Prepared catalyst of Example 3, 0.2 part,

e. 1,1,2,2-Tetrachloro-1,2-difluoroethane, 327.4 parts.

Upon isolation 123.8 parts of the adduct product were recovered.

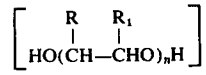
This utilized a mol ratio of A/B of 2.0 and a mol ratio of (A + B)/C of 0.67.

EXAMPLE 20

The procedure of Example 16 was repeated employing the following materials:

a. Fluorocarbamate product of Example 2, 40.6 parts,

b. Polypropylene glycol 1025



where one of R and R_1 is H and the other is methyl, and the molecular weight is about 1,025, 61.2 parts (0.06 mole or 0.12 equivalents),

c. Bis(methoxymethyl)ethylene urea, 24.3 parts (0.04 mole or 0.28 equivalents),

d. Prepared catalyst of Example 3, 0.2 part,

e. 1,1,2,2-Tetrachloro-1,2-difluoroethane, 327.4 parts.

The 110.1 parts of adduct product did not solidify completely, but remained somewhat plastic.

This preparation employed a polypropylene glycol in place of polyethylene glycol. The mol ratio of A/B was 1.33, and the mol ratio of (A + B)/C was 1.0.

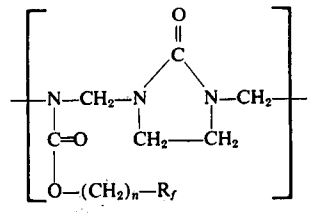
The adduct products of Examples 16–20 were applied to 100% polyester double knit cloth as described in Example 5. In each instance the dried and cured test cloth contained, based on fabric weight, 2.5% of the polymer, 1.0% of the permanent press melamine resin composition (Aerotex 23 Special) and 0.2% of the resin catalyst composition (Accelerator MX). Results of Oil Repellency, Water Repellency and Soil Release Tests initially and after five home washes and dryings are shown in Table IV.

TABLE IV

Adduct Product of Example -	16	17	18	19	20	Untreated Cloth
Initial Water Repellency	0	0	0	0	0	0
Initial Oil Repellency	1	5	6	4–5	5–6	0
Initial Soil Release	67	5	–3	31	27	770
After 5 Home Washes -						
Water Repellency	0	70	0	70	70	70
Oil Repellency	0	1	2	2	0	0
Soil Release	536	104	14	59	667	770

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

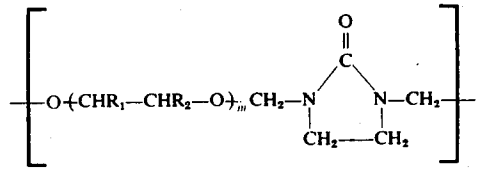
1. An adduct containing units



wherein

n is an integer of from 1 through 12 and

R_f is perfluoroalkyl of from 4 through 16 carbon atoms; and

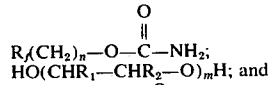


wherein

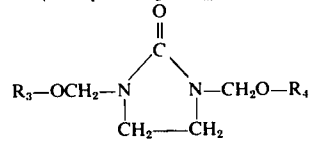
m is an integer of from 10 through 300,

R_1 is hydrogen or methyl and R_2 is hydrogen or methyl with the limitation that at least one of R_1 and R_2 is hydrogen;

prepared by condensing in the presence of an acid catalyst

A) 

B) $HO(CHR_1—CHR_2—O)_mH$; and

C) 

wherein

m, *n*, R_f, R_1 and R_2 are as defined above,

R_3 is alkyl of from 1 through 4 carbon atoms

and R_4 is alkyl of from 1 through 4 carbon atoms;

wherein the molar ratio of A to B is from about 0.25:1 to 9:1, and the molar ratio of A + B to C is from about 0.6:1 to 1.5:1, the condensation being carried out at a temperature of about from 50° to 150°C. to distill from the system alcohol formed by the condensation.

2. An adduct of claim **1** wherein the

A. reactant is a carbamate wherein $n = 2$;

B. reactant is a polyethylene oxide glycol having a molecular weight of from 200 to 4,000; and

C. reactant is the urea wherein R_3 and R_4 are methyl.

3. An adduct of claim **2** wherein the (B) reactant is a polyethylene oxide glycol having a molecular weight of about 1,000 to about 1,800.

4. An adduct of claim **1** wherein the condensation is carried out in an inert diluent.

5. An adduct of claim **2** wherein the condensation is carried out in an inert diluent which forms an azeotrope with methanol.

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